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Surface ionization sources and applications

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Abstract

A series of new instruments have been developed for the study of ion emission from hot inorganic deposits, these being; a tube ion source, an ion source imaging instrument, and an ion/neutral mass spectrometer. Techniques have been developed for applying these instruments to the development of new ion emitters as well as in studying the properties of previously developed emitters. This line of study has led to a new type of anion emitter that has found use as the primary gun for the static SIMS analysis of insulators. Applications of the new primary anion gun to the measurement of environmental contaminants are discussed.

Introduction

Surface ionization (SI) was recognized at least 70 years ago as a scientific phenomenon, and has been employed as an analytical tool for almost 60 years. SI has been investigated in a variety of contexts, but in general this is an area that has been understudied, in spite of the wide spread applications in mass spectrometry for the measurement of isotope ratios. Of the studies that have been conducted on the fundamentals of SI, most have involved the study of atoms striking a pure, hot metal surface. Few have investigated mechanisms of the sublimation of ions from complex deposits. We have been interested for many years in the chemistry of deposits that directly sublime (or evaporate in the case of liquid deposits) ions from the surface. This is a complex field, and after many years we are evolving a series of tools which are helping us to better understand the inorganic and physical chemistry which determines which types of emitters, when heated, will efficiently produce ions. This is not a mature field, however, and could easily accommodate additional investigators.

In the early 1960s the Idaho National Engineering Laboratory (INEL) began a program for the measurement of fission yields for the major fissioning species in a variety of types of nuclear reactors. This led development of methods for performing isotope ratio measurements on a wide range of fission product elements. The culmination of these studies were the Oklo Natural Fission Reactor studies were performed jointly between Los Alamos National Laboratory, Curtin University and the INEL (Loss *et al.* 1988; Curtis *et al.* 1989; Loss *et al.* 1989). The development of new methods for measuring isotope ratios led to an interest in the chemistry of the deposits on the hot filaments which emitted ions. These activities have in turn been developed into a new line of ion guns for use as the primary ion beam in static secondary ion mass spectrometry (static SIMS) for the measurement of environmental pollutants.

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If one studies a variety of ion emitters, over time there will be certain systems which produce ions with unexpectedly high intensity ("boomers"). Examples of this type include (but are certainly not limited to);

1) the alkali metal cations from aluminosilicates (typically, but not always, zeolites) (Beck *et al.* 1989; Satoh *et al.* 1987; Pargellis & Seidl 1978);
2) borate (BO_2^-) from rare earth oxides;
3) perrhenate (ReO_4^-) from barium perrhenate in europium and ytterbium oxide matrices (Delmore *et al.* 1995);
4) halides (Cl^-, Br^-, I^-) from lanthanum hexaboride (Rachidi *et al.* 1976; Delmore 1982).

When one attempts to intentionally produce an emitter which produces ions as efficiently as those which are produced from contaminants, the results can sometimes be disappointing. An example is iodine from lanthanum hexaboride (LaB_6). Iodine present as a contaminant in LaB_6 is ionized with much higher efficiency than any intentionally added for analysis, and similar issues arise with all of the above examples. These are examples of the importance of the chemical form of the element or molecule to be ionized; ionization efficiency can drop dramatically unless the appropriate chemical species is identified and added in that form.

We have chosen to investigate these high intensity "boomers" because they are easier to study, and hence we would be more likely to discover basic features that would lead to fundamental understandings. The two emitters which we have studied the most are alkali metal zeolites and perrhenate/rare earth oxides, and both appear to be "scalable." That is, the intensity of the emitted ions can be increased by increasing the size of the deposit, by increasing the loading of the species to be ionized in the matrix, and by increasing the temperature. This is in contrast to the molten glass ion emitters (silica gel type matrices) which are much more difficult (perhaps impossible) to scale (Huett *et al.* 1995).

There will be three main themes developed in this paper. First, we will concentrate on the two ion emitters that have found use in this laboratory, alkali metal cat-

ions from zeolite, and perrhenate (ReO_4^-) anions from a europium oxide/barium perrhenate ceramic emitter. Second, we will briefly describe two instruments built specifically for the study of these emitters, and methods developed to study these emitters. Third, we describe how these two ion emitters have been incorporated into ion guns used for SIMS instruments, and show that the ReO_4^- anion gun has proven to have great utility for the SIMS analysis of partial monolayers of adsorbates on insulating surfaces.

Experimental procedures

The literature has many references to the emission of alkali metal cations from aluminosilicates, and in practice almost any zeolite will upon heating emit large currents of alkali metal cations. These zeolites can be soaked in aqueous solutions of an alkali metal chloride or nitrate at room temperature and when the material is heated to 700 to 800°C (Beck *et al.* 1989) in vacuum, will emit that particular alkali metal cation. These emitters (for all of the alkali metals) are widely used in ion guns for a variety of applications, and are even sold commercially by several companies.

The perrhenate anion emitter was developed at the INEL and has been used as the active element in several ion guns used for static SIMS. These SIMS instruments have been used for a wide range of analyses, which have opened many new analytical possibilities. The perrhenate anion emitter is a ceramic material, the composition of which is being published elsewhere (Delmore *et al.* 1995), and operates in the range of 800 to 900°C. It can deliver up to 10 nA into a 2mm spot size, but typically is operated at about 100 pA.

Hardware called the "tube ion source" has been used in most of our studies. It entails pressing the powdered emitter material into a tube, spot welding this tube to rhenium ribbons, and then spot welding the ribbons to the posts of a filament support (Delmore *et al.* 1994). The zeolite-based materials were pressed into 304 stainless steel tubes which were pinched off at the back. The perrhenate emitters were pressed into rhenium tubes with a tantalum plug in the back.

Two instruments have been developed for testing the properties of these emitters. These have proven to be very useful in helping to understand the ion formation mechanisms. These instruments are an ion source imaging instrument (Delmore *et al.* 1994) and an ion/neutral mass spectrometer. The ion source imaging instrument utilizes a tube ion source mounted in an imaging lens, and the emitted ions are projected onto a screen where the image can be recorded.

The ion/neutral mass spectrometer is still very early in the development cycle. It employs a source which combines both a surface ionization capability and an electron impact capability for ionizing the neutral gases which are desorbed from the emitter material. A computer system, which is now working for most of the desired functions, is being developed to control the mass scanning, the data collection, correlation and display, and ion source focusing. The focusing voltages for the two ionization modes are very different, and the computer program can step between these modes, so that a clear definition can be made between ions originating from the two ionization modes. The value of this instrument is that it allows both the ion and the neutral components to be individually mass-analyzed so that the relative proportions of ions to neutral components, and the change in the ratio of these components with time, can be measured. This in turn gives insights into ion formation mechanisms, and permits optimization of the emitter being studied. An attempt to quantify the ratios of ions to neutrals has not yet been made.

The perrhenate anion emitter has been incorporated into an ion gun, which in turn has proven to be very useful in static SIMS instruments used for the analysis of insulating materials. There are five static SIMS instruments in our laboratory which use this type of ion gun, two using single quadrupoles (SQSIMS), one using a triple quadrupole (TQSIMS), and two using ion traps (ITSIMS). The SQSIMS have been described elsewhere (Appelhans *et al.* 1987; Appelhans & Delmore 1989; Appelhans *et al.* 1990; Appelhans *et al.* 1994).

Results

Ion Emitters

The ion source imaging instrument has been used quite extensively to image three types of emitters, the two being discussed here (Delmore *et al.* 1994), and molten glass emitters made using the silica gel method (Huett *et al.* 1995). Briefly, the ions were shown to come from the face of the deposit, and not from interfacial regions. This might be obvious in hindsight, but before these imaging measurements were made there was the distinct possibility that the ions could originate from the metal surfaces that supported and surrounded the deposits. The imaging studies demonstrated conclusively that the ions were coming from the face of the deposits, and by inference that the chemical and physical properties of the deposit determined the emitter properties of the system. The substrate (the tube which holds the deposit) served the purpose of supporting the deposit, hopefully, but not always, inertly.

The ion/neutral mass spectrometer has been used to perform a preliminary study of potassium cation emission from zeolites pressed into stainless steel tubes. The alkali metal zeolites are known to be ionic conductors, which means that they conduct electricity with cations which are mobile in the lattice, as opposed to conduction with electrons. These ion emitters are stable and intense emitters of potassium cations. At no time could any neutral species be observed which contained potassium. The only potassium species observable was the atomic cation. This demonstrates that the mobile cations in the solid phase are being desorbed as cations into the gas phase, and that this is a straight-forward example of preformed ions passing from the condensed phase into the gas phase.

We have conducted extensive studies with various perrhenate salts blended with various rare earth oxides (Delmore *et al.* 1995). We have found that the alkaline earth perrhenates are reasonably refractory compounds, and are the only perrhenate salts that give good ion emission when blended with a rare earth oxide. Ba perrhenate is the salt of choice. The best ion emitters by

far are composed of Ba perrhenate in a Eu_2O_3 or Yb_2O_3 matrix. These rare earth oxides are in the +3 oxidation state, but stable +2 oxidation states are available. It is hypothesized that the +3 oxidation states of Eu and Yb can function as mild oxidizing agents since they can be reduced to the +2 state. This in turn helps maintain rhenium as perrhenate, in which rhenium has the maximum oxidation state of +7. An alternate explanation is that the accessibility of the +2 oxidation state allows for a different crystal structure which might enhance ion emission. The Eu oxide matrix gives an order of magnitude more intensity than rare earth oxides like Nd early in the life cycle of the emitter, largely due to the fact that it can be heated to higher temperatures without depleting perrhenate. At the higher temperatures and emission currents, the lifetime of the Eu based emitter is from one to two orders of magnitude longer. This supports the hypothesis that perrhenate is being lost in the Nd host matrix, while it is preserved in the Eu based emitter. If it were related to factors such as work function, or mobility of perrhenate in the host matrix, factors which might be expected to be related to crystal structure, then it would be expected that the intensity at any given time would be different but not that the lifetimes would be so different. We feel that the evidence supports a model where preformed ions are sublimed from the surface (Delmore *et al.* 1995).

SIMS Applications

It has been recognized since the early days of SIMS that when an anion strikes an insulating surface, that electrostatic charging is much less of a problem than when a cation strikes the same surface (Anderson *et al.* 1969). This is because there are more secondary electrons sputtered from the surface than ions, and an electron leaving the surface causes the sample to charge positive, the same as an arriving positive ion. An arriving negative ion tends to balance the lost secondary electrons, greatly reducing the charging rate. The limitation in implementing this concept was the lack of anion guns, with the O^- gun (Anderson *et al.* 1969) the only practical one available. The mass of this ion is so light that its use has been limited. The halide guns have the threat of corroding the vacuum system, since they generally employ elemental halogen (Rachidi *et al.* 1976). Hence most primary ion guns for SIMS have employed cations, with Ar, Xe, Cs and Ga most commonly used. When insulators are to be analyzed, electron flood guns are used to balance surface charging. The balance point between the flux from the cation gun and the flux from the electron flood gun can be a problem with many instruments. This problem is much less severe with TOF-SIMS, however, since the sample can be flooded with electrons when the cation beam is turned off.

The perrhenate anion beam provides great versatility as a primary SIMS gun for the analysis of insulators, especially when combined with the technique of pulsed extraction (Appelhans *et al.* 1990). Also, the heavy mass (250 daltons) provides excellent secondary ion yields, although one-on-one comparisons of secondary ion yields are just now being conducted, and the results of the comparison are not yet published. The extraction voltage applied to the sample, which causes secondary ions to be focused into the mass spectrometer, is reversed about 20 time per second, alternately focusing positive and then negative secondary ions into the mass spectrometer. The duty cycle between positive and negative ion extraction is adjusted to find a charge neutrality point, with ion collection times tied to this duty cycle. This has proven to be a highly efficient method for maintaining charge neutrality on insulating samples.

We have built five static SIMS instruments which employ the perrhenate anion source used with pulsed extraction, and have had remarkable success with the analysis of insulators (Delmore & Appelhans 1991; Groenewold *et al.* 1995a,b,c,d,1996; Ingram *et al.* 1995). The large perrhenate molecular anion has proven to be particularly effective at lifting adsorbate molecules from surfaces. We have analyzed molecules such as the pesticide malathion (Delmore & Appelhans 1991) directly on the surfaces of plant leaves, the extractant tri-n-butyl phosphate adsorbed on soil and rock (Groenewold *et al.* 1995a,b), the indoor air contaminant cyclohexyl amine on dust particles and miscellaneous laboratory objects (Groenewold *et al.* 1996), the degradation products of chemical warfare agents on a variety of surfaces (Ingram *et al.* 1995; Groenewold *et al.* 1995c), and the detection of inorganic complexes on carbon (Groenewold *et al.* 1995d). These analyses are but a few of the many types which these instruments have been able to accomplish.

The analysis of 'salt cake' is one example of the efficacy of the perrhenate primary ion for producing rich inorganic species information. Salt cake is a material which has formed in radioactive waste storage tanks, and there exists an important need for characterization. A synthetic salt cake was prepared minus radio nuclides to simulate actual material, to evaluate different characterization techniques (Bajic *et al.* 1995). The synthetic sample consisted primarily of sodium nitrate, with a significant quantity of nitrite and sodium nickel ferrocyanide. The composition of the sample is described in terms of the relative number of moles added (Table 1).

Table 1

Relative molar composition of synthetic salt cake, normalized to $NaNO_3$.

Comonent	mole fraction
$NaNO_3$	1.000
$NaNO_3$	0.100
$NaNO_3SO_4 \cdot H_2O$	0.010
$Na_2NiFe(CN)_6$	0.220

The anion spectrum was particularly informative regarding inorganic species present in the sample. The most abundant ion in the anion spectrum was CN^-, and relatively abundant Na, Fe and Ni cyanide adduct ions were also readily observable at *m/z* 75^-, 108^-, 110^-, 112^-, 134^-, 136^-, and 138^- (Figure 1; note that the Ni adducts have two major isotopes). Fe and Ni both have two cyanide adduct ions, one each for the +2 oxidation states, and one each for the +3 oxidation states. In addition to the cyanide bearing ions, nitrate/nitrite bearing species were observed at *m/z* 115^-, 131^- and 147^-. These ions correspond to $Na(NO_2)_2^-$, $Na(NO_2)(NO_3)^-$, and $Na(NO_3)_2^-$. What is significant about the observation of these ions is that they were either low abundance, or could not be

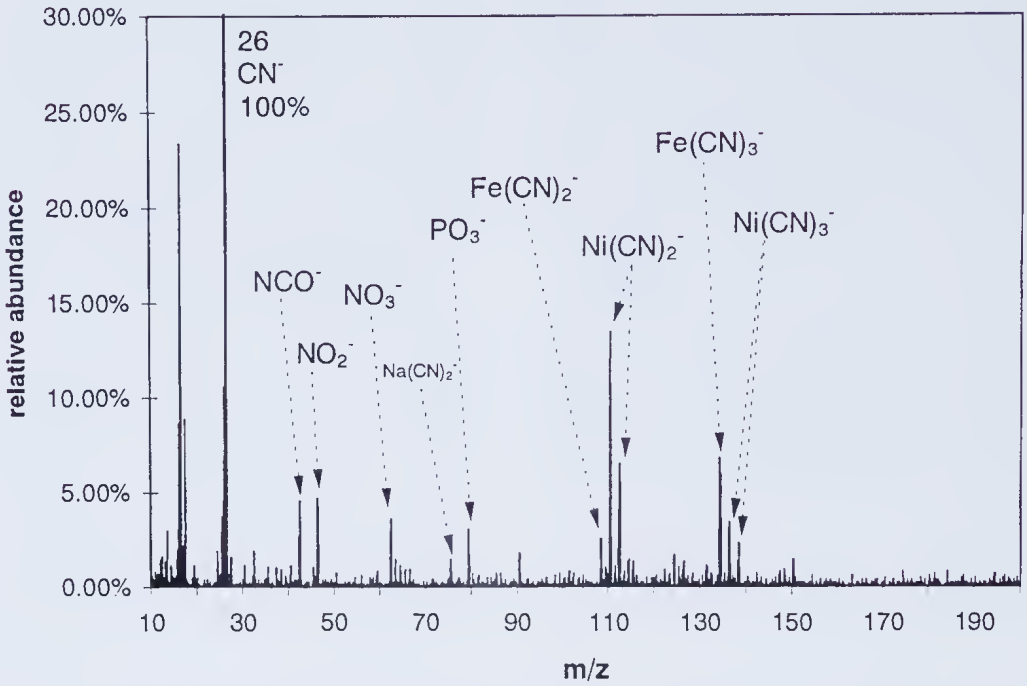

Figure 1. Anion SIMS spectrum from salt cake (described in Table 1). Note the prevalence of complex molecular species in relation to the more simple species.

observed when the sample was analyzed using a SIMS spectrometer equipped with an atomic primary ion gun (Ga^+).

Conclusions

We have studied the chemical and physical characteristics of ion emitting deposits, and have developed unique instrumentation and methods for investigating the nature of these emitters. We feel that the real high intensity "boomers," which give very high ion yields, are probably systems which form ions in the condensed phase prior to emission. While we have gained new insights into these emitters, much remains to be learned. For example, probably many other high intensity ion sources could be developed but have not yet been discovered. There is also the question as to whether europic oxide is truly an oxidizing matrix, or if the ability of this matrix to enhance perrhenate anion emission is due to some other factor. Many such research topics can be envisioned, and they only await study.

The original intent of these studies was to gain new insights into ion emitters so as to allow better isotope ratio analyses for nuclear and geologic studies. This has remained an interest, but in the process emitter systems have been discovered which emit heavy and unusual ions (in particular the perrhenate anion), that have proven to be valuable for the static SIMS analysis of heavily insulating surfaces. The perrhenate anion has proven to be particularly valuable for the analysis of partial monolayers of adsorbed contaminants on insulating surfaces.

This work also demonstrates the extent to which a scientific project can lead to new lines of study, some of which can have practical applications that could never have been predicted. The fission yield studies of 30 years ago have led us through a sequence of programs and studies which today give us the capability to measure environmental pollutants. The common thread that allowed this to occur has been a better understanding of ion emission from hot surfaces.

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